

## Composition Studies on Tobacco XXXIX

### Changes in Smoke Composition and Filtration by Artificial Alteration of Smoke pH: Formic and Acetic Acids and Volatile Phenols\*

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Drastic changes in the pH of cigarette smoke can be made using cigarette additives. These changes are accompanied by alterations in the composition and filtration characteristics of the smoke. By increasing the acidity of smoke in this way, the selective filtration of pyridine by activated charcoal filters is reduced, presumably due to an increased proportion of pyridine in the particulate matter as the salt (1). By alkalinizing the smoke, some selective filtration of nicotine is observed presumably due to an opposite effect, i.e. a higher proportion of free base in the vapor phase (1). Generally, these findings follow the concept that improved filter efficiency can be obtained by increasing the proportion of volatile bases in the vapor phase available for filtration. However, factors other than base-salt equilibria appear to be operative and in some cases, produce unexpected findings, e.g. changes in the pyridine: nicotine ratio in acidified smoke and a slight reduction in selective filtration of pyridine on increasing the pH of the smoke from 6.1 to 7.9 (1).

Some changes in vapor phase constituents also occur when smoke pH is changed in this way (2). Alkalinization of the smoke results in removal of more than 90% of the hydrogen sulfide and hydrogen cyanide from the vapor phase when activated carbon filters are employed. Much of this reduction is apparently due to pH alteration, resulting in shifts in the acid-salt equilibria.

The present study was undertaken to determine the effect of changing smoke pH on the levels and filtration of certain weakly acidic compounds of intermediate volatility, i.e. formic and acetic acids and phenols. Although the volatile phenols were previously believed to contribute to the tumorigenicity of smoke in animals (10, 11), their role in this regard has been questioned recently (12). However, phenol has significant ciliostatic activity (9). Formic and acetic acids are also potent ciliostats when tested in aqueous solution (7). Although much work has appeared on the filtration of phenol from smoke (13), we are aware of no comparable reports on the characteristics of filtration of formic and acetic acids by cellulose acetate and activated carbon filters.

## METHODS

### 1. Cigarettes and Smoking Conditions

Nonfilter and filter cigarettes with or without additives were prepared as previously described (1). Lactic acid (100 mg/cigarette) and dipropylamine (100 mg/cigarette) were employed as the additives to obtain the acidic smoke and alkaline smoke, respectively, in the work involving formic and acetic acids. All cigarettes were smoked under previously detailed conditions (1). For formic and acetic acid determinations, mainstream smoke from the cigarettes was collected on a Cambridge filter followed by a bubbler containing 25 ml water. The filter was changed after 5 cigarettes were smoked, and the water in the bubbler was replaced after 10 cigarettes were smoked.

In the work on the phenols, formic acid was used as the acidic additive (1) and the cigarettes were smoked and the smoke collected by a previously described procedure (1). One Cambridge filter containing the particulate matter from 5 cigarettes was macerated in acetone and the resulting suspension was steam distilled from 1 N  $\text{H}_2\text{SO}_4$  as detailed earlier (1). Two hundred ml of distillate were collected and analyzed for total steam-volatile phenols.

### 2. Analytical Methods

Free formic and acetic acids were determined by a previously published method (8) involving ion exchange separation of the acids from the smoke, *in situ* methylation of the acids on the resin column and gas chromatographic measurement of the methyl formate and methyl acetate eluted from the resin column. For each analysis, the collected smoke from 20 cigarettes (4 Cambridge filters and 2 aqueous traps) was assayed. Five replicate analyses were performed to obtain a final analytical value for each experimental condition.

Total steam-volatile phenols were determined colorimetrically by reaction with diazotized p-nitroaniline (14). Four replicate analyses (representing values for 20 cigarettes) were performed for each experimental condition.

\* Received for publication: 12th August, 1969

with one exception: three analytical values were obtained for cigarettes containing a cellulose acetate filter and formic acid as the acidic additive. Total particulate matter (TPM) and the pH of smoke were determined as described previously (1).

## RESULTS AND DISCUSSION

### 1. Formic and Acetic Acids

Cigarette smoke contains formic and acetic acids present as esters, salts and free acids. The esters exist as volatile or nonvolatile compounds, e.g. isopropyl formate, triacetin, solanesyl acetate, etc. (6). Most methods of quantitative determination of  $C_1$  and  $C_2$  acids in smoke involve steam distillation and/or extraction with aqueous alkali, which may hydrolyze the esters to varying degrees. The method used in the present study apparently does not cause hydrolysis and gives a valid measure of the  $C_1$  and  $C_2$  acids present in both the free acid and salt forms.

The unfiltered smoke from the commercial cigarettes used in the present investigation had a pH of 5.6. The calculated salt:acid ratios for formic and acetic acids at this pH are 71:1 and 7.1:1, respectively, using  $pK_a$  values of 3.75 and 4.75, respectively. Assuming all the free acid is in the vapor phase and passes the Cambridge filter, the amounts of free formic and acetic acids in the aqueous trap should be about 1.4% and 12%, respectively, of the total  $C_1$  and  $C_2$  acids (free form and salts) in smoke from nonfilter cigarettes. Other workers (8) have reported levels of 0% and 8% for the  $C_1$  and  $C_2$  acids in the trap, and these levels were generally confirmed in the present study. Under these conditions, it is unlikely that any gross loss of these acids occurs due to volatility during bubbling of the smoke from successive cigarettes in a standard run. However, when testing the smoke from cigarettes with acidic additives, such loss becomes a possibility. Using cigarettes containing lactic acid, the pH of the smoke is about 4.2 and the calculated salt:acid ratios at this pH are about 2.8:1 and 1:3.6 for the  $C_1$  and  $C_2$  acids, respectively. Under these conditions, relatively large amounts of free acids might be found in the traps and volatility losses might be

significant. Since the cigarettes containing dipropylamine give smoke of pH 8.2 and the trap has a pH of 7.9, another possible analytical error might occur under these conditions, i.e. hydrolysis of  $C_1$  and  $C_2$  esters in the trap or on the filter.

To study these possible errors, the method was modified by adding sufficient alkali to the traps to obtain a pH of 10.0 before smoking. Cigarettes containing lactic acid were then smoked and the traps and filters were analyzed for the  $C_1$  and  $C_2$  acids. No significant difference was found between values obtained with this collection system and one containing water in the traps as prescribed in the original method. In the case of cigarettes containing dipropylamine, no  $C_1$  and  $C_2$  acids were found in the trap, as expected. However, to test the possibility of ester hydrolysis on the filter used to collect the particulate matter, benzyl acetate was added to Cambridge filters which were then soaked in buffer (pH 8.3) for about 1 hour. Analysis of the extract showed 10–18% hydrolysis. In another experiment, 25 mg of benzyl acetate, were placed on a filter and the smoke from 5 cigarettes containing dipropylamine was collected thereon. No significant increase in values for acetic acid was obtained. Considering the levels of known formates and acetates in smoke (3–5) and the levels of these acids subsequently found in the smoke from cigarettes containing dipropylamine (*vide infra*), it appears that hydrolysis of esters contributes little or nothing to the analytical values for  $C_1$  and  $C_2$  and the original method was employed in all analyses.

Table 1 shows representative data on the changes in levels of the acids and in the filtration patterns for smoke from cigarettes with and without additives. In some runs, TPM and acid levels in the smoke from cigarettes with lactic acid were higher than those in Table 1; however, the conclusions discussed below applied equally well in these instances. The levels in the smoke from the control, nonfilter cigarettes were slightly higher than the maximum reported by others for commercial cigarettes using a longer (30 mm) butt length (8). The overall variability of the values was much larger than previously claimed for this analytical method. The average coefficients of variation in the smoke from all cigarettes without additives were 28.6 and 19.8 for formic and acetic acids, respectively.

**Table 1** Effect of acidic and basic cigarette additives on the levels and filtration of formic and acetic acids in smoke

Additive	Filter <sup>1</sup>	Smoke pH	TPM <sup>2</sup> (mg/cig)	Levels (μg/cig) <sup>2</sup>		S values	
				Formic <sup>3</sup>	Acetic <sup>3</sup>	Formic	Acetic
None	None	5.6	24.7 ± 2.0	116 ± 36	412 ± 105	—	—
	CH	6.1	18.8 ± 2.9	73 ± 18	224 ± 47	1.2	1.4
	CA	5.8	14.4 ± 2.7	52 ± 15	229 ± 29	1.3	1.1
Lactic acid	None	4.2	29.9 ± 3.4	75 ± 15	248 ± 26	—	—
	CH	4.2	21.9 ± 3.3	46 ± 28	72 ± 31	1.2	2.5
	CA	4.2	15.6 ± 1.8	22 ± 14	135 ± 24	1.8	1.0
Dipropylamine	None	8.2	38.4 ± 3.4	416 ± 132	1229 ± 124	—	—
	CH	7.9	24.5 ± 3.7	204 ± 51	679 ± 187	1.3	1.2
	CA	7.9	18.4 ± 3.7	142 ± 28	536 ± 88	1.4	1.1

<sup>1</sup>CA = cellulose acetate

CH = cellulose acetate + activated carbon

<sup>2</sup>Average ± 1 std. dev.

<sup>3</sup>Present as free acids and salts

Generally, smoke from cigarettes containing acidic and alkaline additives gave higher values for TPM than the controls due possibly to transference of the additive to the smoke, as previously discussed (1). The overall pattern of TPM values was slightly different than that reported earlier (1) due possibly to changes in the composition of the commercial cigarette blend since the previous investigation. The smoke from cigarettes with lactic acid had somewhat lower levels of formic and acetic acids than the smoke from cigarettes without additives\*. Apparently, the normal pattern of pyrolytic generation or release of the C<sub>1</sub> and C<sub>2</sub> acids is altered through a specific effect due to lactic acid or through a nonspecific pH effect. A similar alteration was observed previously with the pyridine : nicotine ratio in the smoke from cigarettes with an acidic additive (1).

In the smoke from cigarettes containing the alkaline additive, a large increase in C<sub>1</sub> and C<sub>2</sub> acids was observed. This may be due to at least two factors: changes in the patterns of pyrolytic generation and/or release of acids due to pH; or pyrolysis of dipropylamine to yield the C<sub>1</sub> and C<sub>2</sub> acids. On the basis of bond dissociation energies, scission of dipropylamine should be relatively facile; however, oxidation of the fragments to C<sub>1</sub> and C<sub>2</sub> acids in the primarily reducing atmosphere of smoke is less easily explained. Theoretically, scission should be more likely with dipropylamine than lactic acid [b.p. 119° C / 12 mm (d)] which may dehydrate to the more stable acrylic acid (b.p. 141.6° C) during burning.

Evaluation of the filtration characteristics of the C<sub>1</sub> and C<sub>2</sub> acids is more difficult since the large methodological variabilities limit the significance of small differences. The calculated ratio of formate : formic acid in solution at pH 4.2 is about 2.8:1. Using this value and assuming all free formic acid is in the vapor phase, the maximum theoretical S value obtainable for smoke of pH 4.2 would be about 1.4 using the TPM values in Table 1 (CH filter). The obtained S value may indicate that some degree of selectivity occurred. In the case of acetic acid, the calculated acetate : acetic acid ratio in solution at pH 4.2 is about 1:3.6; therefore, if ionization plays a

role in filtration efficiency, acetic acid should offer more potential for selective removal than formic acid at pH 4.2. The maximum theoretical S value based on this ionization at pH 4.2 and the TPM levels (CH filter) in Table 1 would be about 4.5 for acetic acid. The observed S value in Table 1 shows that acetic acid was being removed more effectively than formic acid at pH 4.2 with the multiple filter. However, this pattern was not evident when the activated carbon was removed from the filter. Also, the effect of the carbon filter was not apparent in the smoke from cigarettes without additives. S values larger than 1.0 were obtained with both acids in filtered alkaline smoke; formic and acetic acids in solution at pH 7.9, exist entirely in the salt form for all practical purposes. Considering the methodological variability involved in all of these findings, it can be concluded that a slight degree of selective removal of the acids may exist but the significance is questionable in all but one instance. In smoke from cigarettes with added lactic acid, selective removal of acetic acid is observed using the multiple filter.

## 2. Steam-Volatile Phenols

Data on these components are shown in Table 2. The values for smoke pH and TPM are for the identical cigarettes used in the earlier work on nicotine and pyridine (1). The difference in the patterns of TPM shown in Table 2 have been discussed previously (1). The level of phenols in the control nonfilter cigarette was below the range reported for smoke from American and British cigarettes in a study by other workers (14, 15). This difference was attributed to the longer butt length used in the present study, i.e. 28 mm vs. 23 mm.

The use of formic acid to depress the smoke pH resulted in a large increase in phenols in the smoke from non-filter cigarettes. The additive may not be a major contributor to this increase since formic acid should be a relatively poor pyrolytic precursor of phenols. A similar anomaly involving a shift in the nicotine : pyridine ratio of the smoke was observed earlier (1) with these cigarettes. The level of phenols in the smoke from nonfilter cigarettes with an alkaline additive was in the same range as the control cigarettes.

In the filter cigarettes without additives, some selectivity

\* Probability of difference (18) in formic acid levels for smoke from non-filter cigarettes with and without lactic acid (Table 1) = 0.016.

**Table 2 Effect of acidic and basic cigarette additives on the levels and filtration of steam-volatile phenols in smoke**

Additive	Filter <sup>1</sup>	Smoke pH	TPM <sup>2</sup> (mg/cig)	Phenols <sup>2</sup> (μg/cig)	S values
None	None	5.6	24.2±1.6	187±18	—
	CH	6.1	15.3±0.6	66± 3	1.8
	CA	5.8	17.5±1.3	99±10	1.4
Formic acid	None	4.1	32.0±1.9	289±14	—
	CH	4.9	18.0±0.6	64±28	2.5
	CA	4.4	25.5±2.9	76± 2	3.0
Dipropylamine	None	8.2	30.8±1.1	159±29	—
	CH	7.9	24.7±1.2	122± 6	1.0
	CA	7.9	24.5±0.5	126±11	1.0

<sup>1</sup>CA = cellulose acetate  
CH = cellulose acetate + activated carbon

<sup>2</sup>Average ± 1 std. dev.

was shown by the cellulose acetate filter with or without activated carbon. The presence of carbon appeared to enhance slightly this selectivity; generally, carbon is believed to have a limited selectivity for phenols (13). When the pH of the smoke was reduced by adding formic acid, a significant increase was noted in selectivity for both filters. Conversely, selectivity was lost when the smoke pH was raised to 7.9. At the latter pH, the phenol:phenolate ratio for phenol ( $K_I = 1.28 \times 10^{-10}$ ) in aqueous solution is about 98:1, and ratios for the common methylphenols of smoke that respond to the analytical method are close to this value. The degree of selectivity loss in alkaline smoke is too large to be due entirely to ionization effects. Also, the results with the smoke from cigarettes containing formic acid cannot be explained by a simple rationale involving ionization. At the pH range (5.6–6.1) of the smoke from the control cigarettes, phenol is present almost entirely in the unionized form in aqueous solution and lowering the pH to 4.1–4.9 produces only a negligible difference in the amount of free phenol present therein. The difference in selective filtration for the two acidic pH ranges may involve a single shift in proportion of free phenol in the vapor and particulate phases. At the pH of the smoke from commercial cigarettes, about 20% of the total phenol is believed to exist in the vapor phase (17), but the phenol in the particulate phase is rapidly transferred to the vapor phase as phenol in the latter is removed by filtration. The kinetics of this pattern are apparently altered when an acidic additive is added to the cigarettes resulting in more vapor phase phenol available for filtration. Possibly, the same explanation may be valid for the opposite effect observed in alkaline smoke.

## SUMMARY

The levels of formic and acetic acids in the free acid and salt forms in unfiltered smoke are reduced when smoke pH is lowered from 5.6 to 4.2 using lactic acid as the cigarette additive. The acid levels are increased markedly when unfiltered smoke is alkalized to pH 8.2 using dipropylamine as the cigarette additive. The variability of the analytical method prevented detection of small degrees of selective filtration of the acids. Although indications of selective removal were obtained in smoke of pH 4.2–7.9, using cellulose acetate filters with or without activated carbon, the variability did not permit a firm demonstration of this effect with one exception: a distinct selective removal of acetic acid was observed in smoke of pH 4.2 using a multiple filter. The use of formic acid as a cigarette additive to lower the pH of unfiltered smoke results in a significant increase in the major phenols therein. No change in levels of smoke phenols is observed when dipropylamine is used as a cigarette additive to alkalize the smoke. An increase in selective removal of smoke phenols occurs when smoke pH is depressed from 5.8–6.1 to 4.4–4.9 using filters of cellulose acetate with or without activated carbon. Selectivity is lost when smoke pH is raised to 7.9 using the alkaline cigarette additive.

## ZUSAMMENFASSUNG

Die Anteile der Ameisen- und Essigsäure in der freien Säure- und in der Salzform in ungefiltertem Rauch werden reduziert, wenn der pH-Wert des Rauches unter Benutzung von Milchsäure als Cigarettenzusatz von 5,6 auf 4,2 erniedrigt wird. Der Säureanteil wird merklich erhöht, wenn ungefilterter Rauch unter Benutzung von Dipropylamin als Cigarettenzusatz auf einen pH-Wert von 8,2 alkalisiert wird. Die Schwankung in der analytischen Methode verhindert den Nachweis kleiner Grade einer selektiven Filtration der Säuren. Obgleich Anzeichen für eine selektive Retention aus Rauch vom pH 4,2–7,9 erhalten wurden bei Benutzung von Celluloseacetatfiltern mit oder ohne Aktivkohle, erlaubt die Schwankung keinen sicheren Nachweis dieses Effektes mit einer Ausnahme: Eine deutliche selektive Retention von Essigsäure aus Rauch vom pH 4,2 wurde bei Anwendung eines Mehrfachfilters beobachtet. Der Gebrauch von Ameisensäure als Cigarettenzusatz zur Erniedrigung des pH-Wertes von ungefiltertem Rauch führt zu einem signifikanten Anstieg der wesentlichen Phenole darin. Keine Veränderung im Phenolanteil im Rauch wurde beobachtet, wenn Dipropylamin als Cigarettenzusatz zur Alkalisierung des Rauches benutzt wurde. Ein Anstieg in der selektiven Retention von Rauchphenolen bei Benutzung von Celluloseacetatfiltern mit oder ohne Aktivkohle wird erhalten, wenn der pH-Wert des Rauches von 5,8–6,1 auf 4,4–4,9 erniedrigt wird. Die Selektivität geht verloren, wenn der pH-Wert des Rauches unter Benutzung des alkalischen Cigarettenzusatzes auf 7,9 steigt.

## RÉSUMÉ

Les teneurs de la fumée non filtrée en acides formique et acétique à l'état libre et à l'état de sels sont réduites quand le pH de la fumée est abaissé de 5,6 à 4,2 en employant l'acide lactique comme additif dans la cigarette. Les teneurs en acides sont nettement accrues lorsque la fumée non filtrée est alcalinisée à pH 8,2 en employant la dipropylamine comme additif. La variabilité de la méthode analytique n'a pas permis la détection de faibles degrés de sélectivité dans la filtration des acides. Quoiqu'on ait obtenu l'indication de rétentions sélectives avec une fumée de pH 4,2–7,9, en utilisant des filtres en acétate de cellulose avec ou sans charbon actif, la variabilité n'a pas permis une démonstration probante de cet effet, à une exception près: une rétention sélective évidente de l'acide acétique d'une fumée de pH 4,2 a été observée par un filtre multiple. L'utilisation d'acide formique comme additif dans la cigarette pour abaisser le pH de la fumée non filtrée provoque un accroissement significatif du taux des principaux phénols dans la fumée. On n'observe pas de changement des teneurs en phénols de la fumée quand on utilise la dipropylamine comme additif dans la cigarette pour alcaliniser la fumée. La rétention sélective des phénols par les filtres en acétate de cellulose avec ou sans charbon actif s'accroît lorsque le pH de la fumée est

abaissé de 5,8—6,1 à 4,4—4,9. La sélectivité disparaît lorsque le pH de la fumée est élevé à 7,9 par un additif alcalin dans la cigarette.

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